Monomeric, two-coordinate Mn, Fe and Co(II) complexes featuring 2,6-(2,4,6-trimethylphenyl)phenyl ligands†

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The synthesis and characterization of the monomeric, two-coordinate transition-metal complexes $(2,6\text{-Mes}_2C_6H_3)_2M$ (Mes = mesityl, $2,4,6\text{-Me}_3C_6H_2$, M = Mn, Fe, Co) are reported; $(2,6\text{-Mes}_2C_6H_3)_2Co$ is the first structurally authenticated two-coordinate, homoleptic cobalt(II) complex featuring σ-bonded aryl ligands.

Despite much research interest in transition-metal complexes featuring σ-bonded aryl ligands, two-coordinate homoleptic compounds featuring aryls remain comparatively rare.[1] These coordinatively unsaturated centres are, for most part, found to increase their coordination number by forming aryl bridged oligomers[2–4] or donor/acceptor complexes.[5–7] Bulky *m*-terphenyl ligands have been used to great effect in the stabilization of unusual bonding arrangements and oxidation states, indeed, the synthetic utility of these groups has been demonstrated elegantly by Power and co-workers in the synthesis and crystallographic characterization of the first metal–metal quintuply bonded system $[\{2,6\text{-}(2,6\text{-}^i\text{Pr}_2C_6H_3)_2C_6H_3\}Cr]_2$.[8]

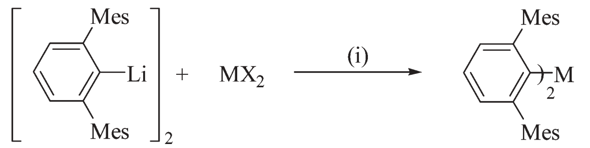
It is only recently that the first homoleptic, two-coordinate transition-metal systems featuring aryl groups have been reported. This was in 1995, when the use of the sterically demanding Mes* ($2,4,6\text{-}^t\text{Bu}_3C_6H_2$) substituent in the stabilization of low-coordinate transition-metal centres was reported independently by two research groups in the synthesis of the structurally authenticated monomeric complexes MMes*_2 (M = Fe, Mn).[9,10] Given the rarity of these two-coordinate aryl complexes and the unusual reactivity displayed by highly unsaturated transition-metal species, we sought to synthesize a number of two-coordinate systems featuring the first-row transition metals with a view to exploring their reactivity. Given the synthetic utility of the bulky *m*-terphenyl $2,6\text{-Mes}_2C_6H_3$ in the stabilization of low-coordinate transition-metal compounds *e.g.* $[(2,6\text{-Mes}_2C_6H_3)Co(\mu\text{-Br})(THF)]_2$ (THF = tetrahydrofuran),[11] we employed this sterically demanding ligand system in the stabilization of the two-coordinate, homoleptic aryl complexes. Herein is described the synthesis, spectroscopic and structural characterization of these compounds.

Reaction of $[2,6\text{-Mes}_2C_6H_3Li]_2$[12] with one equivalent of the metal dihalides $MnCl_2$, $FeCl_2(THF)_{1.5}$ or $CoBr_2(DME)$ (DME = 1,2-dimethoxyethane) at room temperature yields the diaryl species $(2,6\text{-Mes}_2C_6H_3)_2M$ (M = Mn, **1**; M = Fe, **2**; M = Co, **3**),‡ according to Scheme 1. Compounds **1–3** are highly air-sensitive, but can be stored at room temperature under an argon atmosphere for several weeks. The stability of **3** under ambient conditions is contrasted with the Mes* derivative – Wehmschulte and Power have not yet been able to isolate the analogous CoMes*_2 complex.[10] These compounds are thermally stable and have melting points in the range *ca.* 150–240 °C. **1–3** have been identified unambiguously by spectroscopic techniques§ and the results of single crystal X-ray diffraction measurements.¶

Single crystals of **1–3** suitable for X-ray diffraction were obtained by controlled cooling of the saturated hexanes solutions as highly air-sensitive colourless, yellow-green and dark purple crystals, respectively. Complexes **1–3** are isomorphous and feature two crystallographically distinct molecules in the unit cell. The structures of **1–3** feature two-coordinate metal centres bound to two $2,6\text{-Mes}_2C_6H_3$ ligands – the large steric demands of the *m*-terphenyl groups allowing the isolation of the complexes as monomers. This is in contrast with that found for the smaller mesityl ligand, the use of which results in the formation of the trimer $\text{MesMn}(\mu\text{-Mes})_2\text{Mn}(\mu\text{-Mes})_2\text{MnMes}$[2] and dimers $\text{MesM}(\mu\text{-Mes})_2\text{MMes}$ (M = Fe, Co).[3,4] Indeed, complexes **1** and **2** represent rare examples of crystallographically characterized homoleptic, two-coordinate M(II) aryl complexes, and **3** is, to our knowledge, the first example of such a complex featuring Co(II) (Fig. 1). Relevant bond distances and angles for **1–3** can be found in Table 1.

Complexes **1–3** display significant distortion from idealised D_{2d} symmetry with the C–M–C angles for these compounds being in the range 162.8(1)–173.0(1)°. The C–M–C values for **1–3** deviate from the essentially linear coordination displayed by the analogous mercury(II) diaryl $(2,6\text{-Mes}_2C_6H_3)_2Hg$ [C–Hg–C 178.6(3)°][12] and the linear C–Mn–C moiety found in the manganese(II) alkyl complex $Mn[C(SiMe_3)_3]_2$,[14] but are similar to those found in the complexes MnMes*_2 [159.66(10)°][8] and FeMes*_2 [157.9(2)° and 158.9(3)°].[8,9]

The average M–C distances for **1** [2.095(3) Å] and **2** [2.040(3) Å] are consistent with those found for MnMes*_2 [2.108(2) Å] and FeMes*_2 [2.058(4) and 2.051(5) Å].[9,10] As expected, the average



Scheme 1 Synthesis of diaryl complexes $(2,6\text{-Mes}_2C_6H_3)_2M$ (M = Mn, **1**; Fe, **2**; Co, **3**). *Reaction conditions*: (i) toluene–THF, 16 h, −78 °C → room temp., −2 LiX.

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† Electronic supplementary information (ESI) available: Full spectroscopic and crystallographic data for $(2,6\text{-Mes}_2C_6H_3)_2M$ (M = Mn, **1**; M = Fe, **2**; M = Co, **3**). See DOI: 10.1039/b616584b

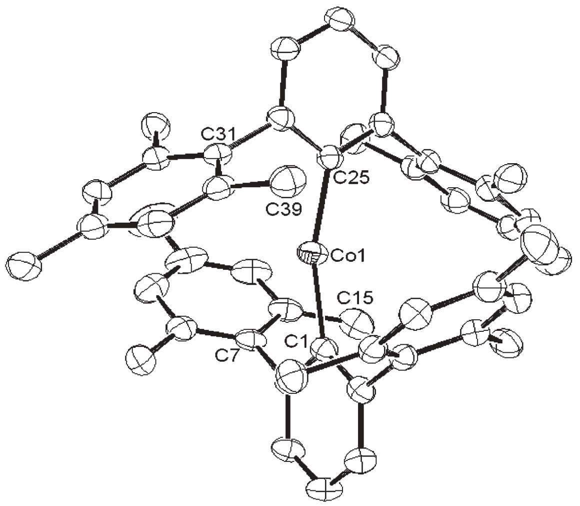

Fig. 1 View of one of the two crystallographically distinct molecules of (2,6-$Mes_2C_6H_3)_2Co$ (**3**) with thermal probability ellipsoids set at the 40% probability level. Hydrogen atoms omitted.

M–C distances decrease in the order **1** > **2** > **3** [**3** = 2.001(3) Å] (reflecting the decrease in ionic radius on going from Mn^{2+} to Fe^{2+} to Co^{2+}).[15] The Co–C distance displayed by **3** is comparable to the terminal Co–C lengths in the dimer $MesCo(\mu\text{-}Mes)_2CoMes$ [1.984(8) Å][1c] and the value for the donor stabilized system *trans*-$(PhEt_2P)_2CoMes_2$ [1.994(3) Å].[6]

Precedent for two-coordinate Co in the solid state exists only for a handful of cases, the coordinatively unsaturated metal centre being stabilized in precedented examples only by the utilization of bulky amido ligands. The solid-state structure of **3** can be compared with those of the amides $Co\{N(SiMePh_2)_2\}_2$,[16] $Co\{N(Ar)BMes_2\}_2$ (Ar = phenyl, mesityl)[17] and the gas-phase structure of $Co\{N(SiMe_3)_2\}_2$.[18] The N–Co–N bond angles for these systems fall in the range 127.1(2)° [$Co\{N(Ph)BMes_2\}_2$] to 180° [$Co\{N(SiMe_3)_2\}_2$] with the N–Co–N angle for $Co\{N(Mes)BMes_2\}_2$ [168.4(1)°] being similar to the C–Co–C angle found in **3** [162.84(10), 172.17(11)°].

The torsion angles between the planes of the two metal-substituted aryl rings in complexes **1–3** are 88.38, 80.83°; 89.75, 80.93° and 89.67, 81.32°, respectively, the lower values being similar to those found in $MMes^*_2$ (M = Mn, 74.5°; M = Fe, 75.5°)[9] and the higher values being similar to that found in the mercury complex (2,6-$Mes_2C_6H_3)_2Hg$ (88.7°).[13] The torsion angles and C–M–C angles for **1–3** differ markedly between the two crystallographically distinct molecules present in these compounds (torsion angles varying by *ca.* 7.5–8.8° and C–M–C angles by *ca.* 6.6–9.3°). It has been proposed that the N–M–N angles in M(II) amide complexes are relatively "soft" and that even weak interactions within these molecules or crystal packing effects can dramatically change this value,[16] these albeit weak effects may provide an explanation of the differences between these values for the two crystallographically distinct molecules for **1–3**. Power has suggested that the bending in the complexes $MMes^*_2$ could be due to weak interactions between the metal orbitals and the *tert*-butyl *ortho*-CH groups of the ligands.[10] On the basis of M–C contacts which are *ca.* 0.7–0.9 Å longer than those reported by Power, any interaction of the metal centres with the *ortho*-CH moieties of the *m*-terphenyl ligands in compounds **1–3** is likely to be very weak. That said, these $M\cdots C_{ortho}$ distances for these complexes are found to be slightly smaller than the sum of their van der Waals radii.[19] A more likely possibility for M–C contacts is that between the metal orbitals and the *ipso*-C atoms of the terphenyl mesityl moieties; the shortest $M\cdots C_{ipso}$ distances for complexes **1–3** are similar to those found by Wehmschulte and Power between the metal atoms and the *tert*-butyl *ortho*-CH groups in $MMes^*_2$.[10]

Solid-state magnetic measurements for **1–3** were measured using a SQUID magnetometer; these compounds are paramagnetic and in the solid state obey the Curie–Weiss law for the temperature range 50–300 K. The magnetic moments for **1–3** are 5.89, 4.90 and 3.81 μ_B and are close to the spin only values, indicating the presence of five, four and three unpaired electrons, respectively. This, together with the almost linear configurations of the complexes correspond to high spin d^5, d^6 and d^7 configurations for **1**, **2** and **3**. The Weiss constants (θ) for these compounds have been determined as 0.49(6), 5.27(8) and 6.20(26) K for **1–3**, respectively, indicating little long-range spin interaction in these systems. Although the discovery of high-spin configurations for complexes **1–3** (for such a relatively strong field ligand as an aryl) seems an unexpected result, the complexes $MMes^*_2$ (M = Mn, Fe) have also been found to exhibit high spin d^5 and d^6 configurations.[9,10]

It is possible to obtain ^1H NMR spectra for these systems; Mn complex **1** displays three very broad peaks which cannot be resolved, but **2** and **3** display a number of paramagnetically shifted peaks in the range −56.2 to +139.0 and −100.2 to +142.6, respectively, which can be assigned to ligand protons.

Table 1 Selected bond lengths (Å) and angles (°) for **1–3**

	(2,6-$Mes_2C_6H_3)_2Mn$ (**1**)	(2,6-$Mes_2C_6H_3)_2Fe$ (**2**)	(2,6-$Mes_2C_6H_3)_2Co$ (**3**)
M–C (av.)	2.095(3)	2.040(3)	2.001(3)
C–M–C	166.41(13), 173.00(13)	164.44(12), 171.06(12)	162.84(10), 172.17(11)
M···C (*ipso*-C of Mes)[a]	2.774(3) (Mn1–C7)	2.720(3) (Fe1–C7)	2.679(2) (Co1–C7)
	2.954(3) (Mn1–C31)	2.915(3) (Fe1–C31)	2.853(2) (Co1–C31)
	2.836(3) (Mn2–C55)	2.751(3) (Fe2–C55)	2.740(2) (Co2–C55)
	3.007(3) (Mn2–C79)	3.004(3) (Fe2–C79)	2.965(2) (Co2–C79)
M···C (*ortho*-CH of Mes)[a]	3.462(4) (Mn1–C15)	3.372(4) (Fe1–C15)	3.362(3) (Co1–C15)
	3.444(4) (Mn1–C39)	3.464(4) (Fe1–C39)	3.436(3) (Co1–C39)
	3.701(4) (Mn2–C63)	3.658(4) (Fe2–C63)	3.660(3) (Co2–C63)
	3.501(4) (Mn2–C87)	3.496(3) (Fe2–C87)	3.423(3) (Co2–C87)
Ar–Ar torsion angle[b]	88.38, 80.83	89.75, 80.93	89.67, 81.32

[a] For clarity, only the four shortest M···C distances are included. [b] Defined as the angle between the planes of the two metal-substituted aryl rings.

Complexes **1** and **2** represent rare examples of monomeric, two-coordinate, homoleptic Mn(II) and Fe(II) complexes featuring aryl ligands, and **3** is the first such example of a complex to contain Co(II), stabilized by very bulky *m*-terphenyl substituents. Studies of the reactivities of these compounds will be reported in due course.

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Notes and references

‡ In a typical reaction, a solution of $[2,6\text{-Mes}_2C_6H_3Li]_2$ (0.225 g, 0.33 mmol) in toluene (10 cm^3) was added dropwise to a stirred suspension of $CoBr_2(DME)$ (0.108 g, 0.33 mmol) in a mixture of toluene (10 cm^3) and THF (2 cm^3) at −78 °C, the resulting mixture warmed slowly to room temperature and stirred overnight. Filtration, removal of volatiles *in vacuo* and extraction into hexanes (15 cm^3), followed by controlled cooling to −35 °C yielded $(2,6\text{-Mes}_2C_6H_3)_2Co$ (**3**) as dark purple crystals of a quality suitable for X-ray diffraction (0.110 g, 48%).

§ Characterizing data for **1–3**. **1**: Mp 240–250 °C (from hexane, melts and turns black). ^1H NMR (300 MHz, C_6D_6, Me_4Si) δ 10.5 (s, br, obscured by benzene peak), 16.9 (s, br, $\Delta\nu_{1/2}$ = 904 Hz), 27.4 (s, vbr, $\Delta\nu_{1/2}$ = 2000 Hz). $\mu_{eff} = 5.89\ \mu_B$. UV/vis (hexane): strong absorption between 200 and 400 nm ($\varepsilon > 1 \times 10^5$ $dm^3\ mol^{-1}\ cm^{-1}$). EI-MS: M^+ = 681 (10%), fragment ion peaks at *m*/*z* 368 $[(2,6\text{-Mes}_2C_6H_3Mn)^+, 25]$, 313 $[(2,6\text{-Mes}_2C_6H_3)^+, 20]$, 298 $[(2,6\text{-Mes}_2C_6H_3 - Me)^+, 20]$, 283 $[(2,6\text{-Mes}_2C_6H_3 - 2Me)^+, 20]$, 268 $[(2,6\text{-Mes}_2C_6H_3 - 3Me)^+, 15]$, 253 $[(2,6\text{-Mes}_2C_6H_3 - 4Me)^+, 10]$; exact mass: calc. 681.3288, found 681.3283. **2**: Mp 200–210 °C (from hexane, melts and turns black, darkens at 140 °C). ^1H NMR (300 MHz, C_6D_6, Me_4Si) δ −56.2 (s, br, $\Delta\nu_{1/2}$ = 205 Hz, 8H, *m*-H of Mes), −36.2 (s, br, $\Delta\nu_{1/2}$ = 1242 Hz, 24H, *o*-CH_3 of Mes), −11.6 (s, $\Delta\nu_{1/2}$ = 38 Hz, 12H, *p*-CH_3 of Mes), 33.7 (s, br, $\Delta\nu_{1/2}$ = 269 Hz, 2H, *p*-H of C_6H_3), 139.0 (s, br, $\Delta\nu_{1/2}$ = 950 Hz, 4H, *m*-H of C_6H_3). $\mu_{eff} = 4.90\ \mu_B$. UV/vis (hexane): strong absorption between 200 and 400 nm; shoulders at λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 353 (1313), 366 (1107), 382 (738), peak at 411 (517). EI-MS: M^+ = 682 (95%), fragment ion peaks at *m*/*z* 369 $[(2,6\text{-Mes}_2C_6H_3Fe)^+, 10]$, 313 $[(2,6\text{-Mes}_2C_6H_3)^+, 60]$, 298 $[(2,6\text{-Mes}_2C_6H_3 - Me)^+, 30]$, 283 $[(2,6\text{-Mes}_2C_6H_3 - 2Me)^+, 40]$, 268 $[(2,6\text{-Mes}_2C_6H_3 - 3Me)^+, 40]$, 253 $[(2,6\text{-Mes}_2C_6H_3 - 4Me)^+, 35]$; exact mass: calc. 682.3256, found 682.3251. **3**: Mp 148–155 °C (from hexane, melts and turns black). ^1H NMR (300 MHz, C_6D_6, Me_4Si) δ −100.2 (s, br, $\Delta\nu_{1/2}$ = 320 Hz, 8H, *m*-H of Mes), −74.3 (s, br, $\Delta\nu_{1/2}$ = 1535 Hz, 24H, *o*-CH_3 of Mes), −29.6 (s, br, $\Delta\nu_{1/2}$ = 109 Hz, 12H, *p*-CH_3 of Mes), 142.6 (s, br, $\Delta\nu_{1/2}$ = 889 Hz, 4H, *m*-H of C_6H_3), *p*-H of C_6H_3 not observed. $\mu_{eff} = 3.81\ \mu_B$. UV/vis (hexane): strong absorption between 200 and 400 nm; shoulder at λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 385 (2017), peak at 521 (497). EI-MS: M^+ = 685 (25%), fragment ion peaks at *m*/*z* 373 $[(2,6\text{-Mes}_2C_6H_3Co)^+, 20]$, 313 $[(2,6\text{-Mes}_2C_6H_3)^+, 55]$, 298 $[(2,6\text{-Mes}_2C_6H_3 - Me)^+, 80]$, 283 $[(2,6\text{-Mes}_2C_6H_3 - 2Me)^+, 25]$, 268 $[(2,6\text{-Mes}_2C_6H_3 - 3Me)^+, 20]$, 253 $[(2,6\text{-Mes}_2C_6H_3 - 4Me)^+, 5]$; exact mass: calc. 685.3239, found 685.3239.

¶ *Crystallographic data* for **1–3**. **1**: $C_{48}H_{50}Mn$, $M_r = 681.85$, $T = 150$ K, $\lambda = 0.71073$ Å, monoclinic, $P2_1/c$, $a = 10.5378(2)$, $b = 38.4153(7)$, $c = 19.0976(4)$ Å, $\beta = 91.6501(8)$, $U = 7727.7(3)$ Å^3, $Z = 8$, $D_c = 1.172$ Mg m^{-3}, $\mu = 0.373$ mm^{-1}; 53601 reflections measured, 15914 unique ($R_{int} = 0.066$), no. of observed reflections 8184 ($I > 2\sigma(I)$); $R = 0.0575$, $wR = 0.0641$ for observed unique reflections [$F^2 > 2\sigma(F^2)$]. Min. and max. residual electron densities: −0.28 and 0.39 e Å^{-3}. **2**: $C_{48}H_{50}Fe$, $M_r = 682.77$, $T = 150$ K, $\lambda = 0.71073$ Å, monoclinic, $P2_1/c$, $a = 10.4641(2)$, $b = 38.4046(3)$, $c = 19.1887(2)$ Å, $\beta = 92.1247(3)$, $U = 7706.05(18)$ Å^3, $Z = 8$, $D_c = 1.177$ Mg m^{-3}, $\mu = 0.423$ mm^{-1}; 84689 reflections measured, 17822 unique ($R_{int} = 0.068$), no. of observed reflections 8216 ($I > 3\sigma(I)$); $R = 0.0463$, $wR = 0.0512$ for observed unique reflections [$F^2 > 2\sigma(F^2)$]. Min. and max. residual electron densities: −0.45 and 0.38 e Å^{-3}. **3**: $C_{48}H_{50}Co$, $M_r = 685.86$, $T = 150$ K, $\lambda = 0.71073$ Å, monoclinic, $P2_1/c$, $a = 10.4123(2)$, $b = 38.5032(6)$, $c = 19.1871(3)$ Å, $\beta = 92.4695(6)$, $U = 7685.1(2)$ Å^3, $Z = 8$, $D_c = 1.185$ Mg m^{-3}, $\mu = 0.478$ mm^{-1}; 55484 reflections measured, 17289 unique ($R_{int} = 0.047$), no. of observed reflections 9572 ($I > 3\sigma(I)$); $R = 0.0452$, $wR = 0.510$ for observed unique reflections [$F^2 > 2\sigma(F^2)$]. Min. and max. residual electron densities: −0.32 and 0.31 e Å^{-3}. CCDC 627379–627381. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616584b

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